

TEMKIN, M.I.

USSR/Chemistry - Catalysts

May 52

"Reduction of a Catalyst With Atomic Hydrogen," S. L. Kiperman, N. A. Pybakova,
M. I. Temkin, Phys Chem Inst imeni L. Ya. Karpov, Moscow

"Zhur Fiz Khim" Vol. XXVI, No 5 pp 621-623

Reduction of wolframic acid anhydride with atomic hydrogen at low temps produces a W catalyst for ammonia synthesis which shows a higher activity at atm pressure than W catalysts obtained by ordinary reduction at high temps.

219T3

TEMKIN, M. I.

USSR Chemistry - Electrochemistry

Thermodynamics

Jun 52

"Thermoelectric and Thermodiffusion Phenomena in Electrolyte Solutions," A.V. Khoroshin, M.I. Temkin, Phys Chem Inst imeni L.Ya. Karpov, Moscow

"Zhur Fiz Khim" Vol XXVI, No 6, pp 773-786

Measured the initial thermoelectromotive forces for silver, silver chloride, and quinhydrone electrodes using various electrolytes and mixts of electrolytes of various concns. On the basis of the results of these measurements, the applicability of Thomson's 1st eq to galvanic,

22025

thermopairs was confirmed. Using the exptl data obtained and published data, calcd std entropies of a number of ions in motion. Calcd Soret's coeffs of a number of electrolytes on the basis of thermo electromotive forces and compared the values obtained in this manner with the results of direct measurements. Demonstrated that the entropy of hydration of moving ions is inversely proportional to the magnitudes of crystallographic ion radii.

22025

TEINKIN, M. I.

Chemical Abst.
Vol. 48 No. 8
Apr. 25, 1954
Analytical Chemistry

6
Direct determination of oxygen in bituminous coal
I. I. Vinogradova and L. M. Kiperman. *Tr. Chirurg. i
Tehn. Gruzinsk. Krem. No. 132*, 15pp. (1952) (English
summary).—A modified Unterzaucher's method, as re-
ported by Alusic, *et al.* (*C.A. 41*, 4407e), for direct detn. of
O in org. compds. was adapted to bituminous coal. An
enlarged app. for larger samples and a metallic Ag absorber
for the removal of H₂S were used. The results obtained by
direct detn. are closer to the actual O content than results
obtained by calen. 33 references. P. J. Hendel

Determination of small quantities of nitrogen in gases.
A. E. Romanushkin, S. L. Kiperman, and M. I. Teinkin
(Phys.-Chem. Inst., Moscow). *J. Anal. Chem. (U.S.S.R.)*
7, 751-2 (1952) (Engl. translation).—See *C.A. 47*, 2037d.
H. L. H.

"APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220009-0

APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220009-0"

Equilibrium between the gas and liquid phases in the system P_2O_5 - H_2O . A. I. Gel'fshtein and M. L. Temkin. Zhur. Osnchekh. Khim. 23, 1795-1803 (1959). - A new method is described for measurement of vapor pressure ($v.p.$) which uses the liquid whose $v.p.$ is to be determined as the manometer fluid. The temps. at which the $v.p.$ equals 1 atm. were determined over a range of compns. 20.0-60.0 wt. % P_2O_5 . A point of inflection on this isobar corresponds to the compnd $H_2P_2O_7$ (72.4% P_2O_5). The relation of the $v.p.$ to temp. for acids in org. solvs. to 70% $H_2P_2O_7$ were found over a $v.p.$ range from 100-1000 mm. The values of $v.p.$ in the P_2O_5 -water system are given for the first time.

"APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220009-0

FRUMKIN, A.N.; GERASIMOV, Ya.I.; CHMUTOV, K.V.; TEMKIN, M.I.;
ZHUKHOVITSKIY, A.A.; TURKEL'TAUB, N.M.

Kirill Alekseevich Gol'bert. Zhur.fiz.khim. 37 no.1:249 Ja
'63. (MIRA 17:3)

APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220009-0"

TEMKIN, M. I.

USSR/Chemistry - Iron-Carbon Catalysts May 53

"Concerning the Magnetic Properties and Structure
of Iron-Carbon Catalysts," M.I. Temkin and S.L.
Kiperman

Zhur Fiz Khim, Vol 27, No 5, pp 753-760

The authors subject to criticism the theory of
active "ensembles" set forth by V.B. Yevdokimov,
I.N. Ozeretskovskiy and N.I. Kobozev. They state
that the work of Kobozev et al actually confirms
their own conclusion, to wit, the Fe on C is found
in the form of small crystals which are spontane-
ously magnetized under the influence of the

273P18

molecular field. The authors reject the assertion
of Kobozev et al that the Fe on C is found in an atomic,
non-crystal-line state.

TEMKIN, M. I.

Aug 53

USSR/Chemistry - Ammonia

"Equilibrium in the Reaction of Hydrogen With Nitrogen Adsorbed on Iron," A. Ye. Romanushkina, S. L. Kiperman, and M. I. Temkin, Physico-Chem Inst im L. Ya. Karpova, Moscow

Zhur Fiz Khim, Vol 27, No 8, pp 1181-1194

The equilibrium that develops as a result of the chem reaction bet substances in the gaseous phase and adsorbed substances, plays an important part in catalytic processes. A method for studying the adsorption-chem equil between N_2 adsorbed on iron and H_2 and NH_3 in the gaseous phase has been developed. Results of measurements at the temp 300, 350, and 400° and $6.7 \cdot 10^{-3}$ atms of N_2 pressure are described.

271T21

TEMKIN, M. I.

21 Jun 53

USSR/ Chemistry - Isotopes, Reaction Kinetics

"Exchange of Oxygen Isotopes between Carbon Monoxide and Carbon Dioxide Over Ferric Oxide Catalyst," H. V. Kul'kova, Z. D. Kuznets, M. I. Temkin

DAN SSSR, Vol 90, No 6, pp 1067-1070

Studied the exchange of O^{18} between CO and CO_2 , over a Fe_2O_3 catalyst and derived an equation giving the rate of the reaction. Presented by Acad A. N. Frumkin 11 Apr 53.

USSR/Physics - Chemistry

Card 1/1 : Pub. 147 - 24/27

Authors : Kabanov, B. N., and Temkin, M. I.

Title : The problem concerning the sign of the electrode potential and electromotive force

Periodical : Zhur. fiz. khim. 28/12, 2258-2261, Dec 1954

Abstract : Discussion was held on the disunity in Soviet and foreign literature regarding the adoption of a unified sign for the electrode potential and electromotive force. It is believed that a complete clarity in designations could be attained by adopting a terminology close to the one used in the I. E. Tamm course. Five references ; 2 USA and 3 USSR (1936-1954).

Institution :

Submitted : July 27, 1954

TEMKIN, M. I.

LUR'YE, G. E., redaktor; BORESKOV, G. K., redaktor; NAHEREZHNYKH, M. Ye.,
redaktor; PSHEZHETSKIY, S. Ya., redaktor; SLIN'KO, M. G., redaktor;
TEMKIN, M. I., redaktor; CHEREDNICHENKO, V. M., redaktor; SHPAK, Ye. G.,
tekhnicheskiy redaktor

[Heterogeneous catalysis in the chemical industry; papers from the
All-Union Conference, 1953] Geterogennyi kataliz v khimicheskoi
promyshlennosti; materialy Vsesoiuznogo soveshchaniia 1953 goda.
Moskva, Gos. nauchno-tekhn. izd-vo khim. lit-ry, 1955. 494 p.
(MLRA 9:2)

1. Russia (1923- U.S.S.R.) Ministerstvo khimicheskoy promyshlen-
nosti. (Catalysis)

The reactivity and the mutual effect of adsorbed atoms and radicals. M. I. Tepkin. *Voprosy Kataliz.* 1963, 1, 103. *Kadzha i Reaktsii v Sverkotvrdosti*. Akad. Nauk SSSR 1955, 484-95.—Recent ideas about the catalytic activity of solid surfaces and the interaction of adsorbed atoms are summarized, and the surface electro-gas model and the reactivity of adsorbed atoms are discussed. The increased interest in the phys. basis of catalytic processes, which may lead to new discoveries in the theory and application of catalysis, is emphasized. W. M. Sternberg

PM

TEMKIN, M.I., FRUMKIN, A.N.

Activation energy of the hydrogen-ion discharge. Zhur.fiz.khim.
(MLRA 9:3)
29 no.8:1513-1526 Ag '55.
(Hydrogen) (Electrolysis)

"APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220009-0

APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220009-0"

Ternikin, M. I.

6

The nature of slow gas sorption by solids. M. I. Ternikin
and N. V. Kul'kova. *Zh. fiz. khim.* 44, No. 5, 1970, p. 1103. (1970) The sorption of a monolayer of O by
porous Ag, obtained by decompostion of $AgCl(s)$, was accom-
plished in 10 min. at 0.2 mm. Hg pressure. For the fuline
ring 100 hrs. the sorption continued at the rate of 0.016
single mol. layer/hr. Some additional sorption could be ob-
served even after 185 hrs. It was concluded that a 2nd ad-
sorption type can occur, in addition to the commonly recog-
nized phys. adsorption, owing to van der Waals forces, and
during the "deep chem. adsorption" Ag lattice changes
phenomenon is believed to be important in heterogeneous
catalysis. A similar form of adsorption is visualized
by the Fe catalyst for N₂H₄ synthesis, the Ni hydrogenation
catalyst, and in gas catalized phenomena. W. M. S.

Revs
PM

Temkin, M. I.

USSR/Physical Chemistry - Solutions. Theory of Acids and Bases, B-11

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 488

Author: Gel'bahteyn, A. I., Shcheglova, G. G., and Temkin, M. I.

Institution: None

Title: Acidity of Aqueous HCl Solutions and of the System $P_2O_5-H_2O$ at Various Temperatures

Original Periodical: Zh. neorgan. khimii, 1956, Vol 1, No 2, 282-297

Abstract: The indicator method was used in determining the dependence of the acidity H_o on the temperature and on the concentration in aqueous solutions of HCl (up to 6.44 M), aqueous solutions of H_3PO_4 (up to 100%), and in strong phosphoric acids containing up to 83.8 wt percent P_2O_5 . It was found that in the system $P_2O_5-H_2O$ the value of H_o passes through a maximum at 79.7 wt percent P_2O_5 , which corresponds to the composition $H_4P_2O_7$. A further increase in the P_2O_5 content of the system leads to a decrease in acidity. Raising the temperature (20-80°) increases the acidity of aqueous HCl solutions. The acidity of

Card 1/2

USSR/Physical Chemistry - Solutions. Theory of Acids and Bases, B-11

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 488

Abstract: the system $P_2O_5-H_2O$ decreases when the temperature is increased (4-40°). In the region of strong phosphoric acids and high HCl concentrations, the derivative of the acidity-temperature characteristic is practically independent of the concentration. The values of the standard change in enthalpy ΔH° and entropy ΔS° during the ionization of the various basic indicators have been calculated.

Card 2/2

Temkin, M. I.

USSR/Physical Chemistry - Solutions. Theory of Acids and Bases, B-11

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 485

Author: Gel'bshteyn, A. I., Shcheglova, G. G., and Temkin, M. I.

Institution: None

Title: Acidity of the System $H_2SO_4-H_2O$ at Various Temperatures

Original Periodical: Zh. neorgan. khimii, 1956, Vol 1, No 3, 506-515

Abstract: The acidity of sulfuric acid was studied as a function of the concentration (4-100% H_2SO_4) and the temperature (20, 40, 60, and 80°). It was established that in solutions containing less than 30% H_2SO_4 by weight, the acidity increases with temperature; in solutions containing 30-50 wt. percent H_2SO_4 , the acidity is practically independent of the temperature, and in solutions with higher concentrations, the acidity decreases with increasing temperature. An equation is given for the acidity: $H_2SO_4:H_0 = -1.74 - \lg K_2 - \lg x_{H_2SO_4}/x_{HSO_4} - \lg f_{H_2SO_4}^f B/f_{HSO_4}^f B^+$, where K_2 is the equilibrium

Card 1/2

USSR/Physical Chemistry - Solutions. Theory of Acids and Bases, B-11

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 485

Abstract: constant for the reaction $H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$; x_1 is the mole fractions and f_1 , the activity coefficients. This equation is equivalent to the equation introduced by Brand (J. C. D. Brand, J. Chem. Soc., 1950, 997). A theoretical discussion of the determination of the acidity of concentrated H_2SO_4 solutions is given. It is noted that the effect of the temperature dependence of the acidity on the rate of reactions which are catalyzed by the acids is comparable to the effect of the temperature dependence of the probable activation energy. Hence, the study of the temperature dependence of the acidity will lead to the correct determination of the activation energy during catalysis by strong acids.

Card 2/2

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APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220009-0"

TEMKIN, M.I.; FRUMKIN, A.N.

On the paper by O.M.Pelterak "The activation energy of hydrogen ion discharge and the problem of absolute potential in electrochemical kinetics". Zhur.fiz.khim.30 no.5:1162-1168 My '56.
(MIR 9:9)

(Hydrogen) (Potential, Theory of) (Pelterak, O.M.)

SHISHKOVA, V.N., kand.khim.nauk; SIDOROV, I.P., kand.tekhn.nauk; TEMKIN,
M.I., doktor khim.nauk

Study of the kinetics of ammonia synthesis by the recirculation
process at high pressures. Trudy GIAP no.7:62-78 '57.
(MIRA 12:9)

(Ammonia)

Temkin, M. I.

Category: USSR / Physical Chemistry - Electrochemistry.

B-12

Abs Jour: Referat Zhur-Khimija, No 9, 1957, 30132

Author : Temkin M. I., Frumkin A. N.

Inst : not given

Title : Comments on the Dependence of Hydrogen Overvoltage on Nature of
the Cathode in Connection with the Paper by Ryuchi and Delae
(Ryutshi and Delakhey in the Original).

Orig Pub: Zh. fiz. khimii, 1956, 30, No 8, 1885-1888

Abstract: A discussion article (RZhKhim, 1956, 12527); see also RZhKhim, 1956,
54066.

Card : 1/1

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"APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220009-0

APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220009-0"

TEKIN, M. I. (Prof.) and APEL'BAUM, L. E.

"The Chain Characteristics of Heterogeneous Catalytic Reactions."

report presented at Scientific Conference at the Inst. for Physical Chemistry
imeni L. Ya. Karpov, Acad. Sci. USSR, Nov 1957.

TEMKIN, M.I., professor.

Applying the kinetics of ammonia synthesis in technical calculations.
(MIRA 10:6)
Khim. nauka i prom. 2 no.2:219-223 '57.
(Chemical reaction, Rate of)
(Ammonia)

"APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220009-0

APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220009-0"

"APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220009-0

APPROVED FOR RELEASE: 07/16/2001

CIA-RDP86-00513R001755220009-0"

GEL'BSHTEYN, A.I. (Moscow); TEMKIN, M.I. (Moscow)

Kinetics of the chemical interaction between ethylene and propylene
with sulfuric acid [with summary in English]. Zhur. fiz. khim.
31 no.12:2697-2705 D '57. (MIRA 11:4)

1. Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moskva.
(Ethylene) (Propylene) (Sulfuric acid)

TEMKIN, M.I.
USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-
chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimiya, No 3, 1958, 7253.

Author : V.M. Cherednichenko, M.I. Temkin.

Inst : Kinetics of Catalytic Synthesis of Methanol.

Title : Kinetics of Catalytic Synthesis of Methanol.

Orig Pub: Zh. fiz. khimii, 1957, 31, No 5, 1072-1090.

Abstract: The kinetics of CH_3OH synthesis of CO and H_2 in a circulation system at 184 to 302° under the pressure of 112 to 640 mm of merc. column and in presence of oxide Zn-Cr catalyst was studied. The reaction rate ω answers the equation $\omega = k_1 \text{CH}_2 \text{CO}^{0.6} / \text{CCH}_3\text{OH} \dots$ (1), k_1 is a constant, CH_2 , CO and CCH_3OH are the concentrations of the reaction components at the interior catalyst surface. The apparent activation energy is 32 kcal per mole. The reaction proceeds in the kinetic range, if the catalyst grain dimensions were 0.7 mm, and it proceeds

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Card : 1/2

USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-
chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimiya, No 3, 1958, 7253.

in the interior-diffusion range, if the grain dimensions were 4 mm; in the latter case, the reaction rate is slowed down by Knudsen diffusion of CH_3OH in the catalyst pores (size about 20 Å). The CO_2 yield at the secondary reaction $2\text{CO} = \text{CO}_2 + \text{C}$ is proportional to the contact duration and does not depend on the catalyst grain size and on CH_3OH , and it rises at the increase of CO . According to a computation, the process is carried out under industrial conditions in the transitory range between the kinetic and the interior-diffusion ranges. As the authors point out, the equation (1) agrees qualitatively with the assumption that the reaction rate is determined by the rate of CO or H_2 adsorption rate, and that the slowing down of the reaction by methanol is caused by the establishing of the adsorption-chemical equilibrium CO (ads) + H_2 (gas) $\rightleftharpoons \text{CH}_3\text{OH}$ (gas).

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TEMKIN, M. I.

76-12-14/27

AUTHORS:

Gel'bshteyn, A. I., Temkin, M. I.

TITLE:

Kinetics of the Chemical Interaction of Ethylene and Propylene with
Sulfuric Acid (Kinetika khimicheskogo vzaimodeystviya etilena i
propilena s seryoy kislotoy)

PERIODICAL:

Zhurnal Fizicheskoy Khimii, 1957, Vol. 31, Nr 12, pp. 2697-2705 (USSR)

ABSTRACT:

The kinetics of reaction with the absorption of ethylene and propylene by sulfuric acid in the diffusion range was investigated here. The velocity of olefin absorption by the immovable liquid layer of great thickness under the constant pressure of the absorbing gas was measured. The problem investigated here can be formulated as follows: a gas dissolves in an immovable liquid and enters into reaction with the same, taking place at a velocity proportional to the concentration. The term which connects the observed speed of absorption with the constants of velocity of the chemical reaction is looked for. It is assumed that the absorption takes place with a great liquid excess. The reaction velocity between gas and liquid can therefore be expressed by an equation of first order. Further, it is assumed that the equilibrium between the gas phase and the liquid layer immediately adjacent to it sets suddenly and follows Henry's law. Provided that the thickness of the liquid

Card 1/3

Kinetics of the Chemical Interaction of Ethylene and Propylene
with Sulfuric Acid

76-12-14/27

layer is sufficiently great, the stationary process, which is characterized by the constant of velocity of absorption, takes place after expiration of a certain initial period. The steady velocities with the absorption of ethylene and propylene by the aqueous solutions of sulfuric acid of various concentrations were measured. That measurement was effected at a sulfuric acid concentration of from 85.3 to 97.2 % by weight with the absorption of ethylene and of from 68.0 to 87% by weight of that of propylene. Taking account of the diffusion laws, the equations for the velocities of gas absorption by an immovable liquid are derived here with respect to the above mentioned case. (The absorption is accompanied by a chemical reaction between the liquid and the absorbed gas). The constants of velocity with the chemical interaction of ethylene and propylene with sulfuric acid under various conditions were determined here from the steady speeds of absorption. Both the apparent, and real values, viz. those which take account of the temperature dependence of acidity, for the activation energy and for the multiplicand before the exponential function, were determined. It is shown that the difference in reactivity with ethylene and propylene is caused by the difference of activation energy of the corresponding reactions. It is shown that the real multiplicand before the

Card 2/3

Kinetics of the Chemical Interaction of Ethylene and Propylene
with Sulfuric Acid

76-12-14/27

exponential equation does not depend on the acid concentration and that it is equal with ethylene and propylene. It is further shown that the lack of a strict proportionality between the constants of velocity and the acidity of the activation energies are dependent on the composition of the acid medium. There are 1 figure, 2 tables, and 14 references, 7 of which are Slavic.

ASSOCIATION: Physical-Chemical Institute imeni, L.Ya. Karpov, Moscow (Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moscow)

SUBMITTED: November 15, 1956

AVAILABLE: Library of Congress

Card 3/3

SOV/81-59-16-56444

Translation from: Referativnyy zhurnal. Khimiya, 1959, Nr 16, p 65 (USSR)

AUTHORS: Temkin, M. I., Apel'baum, L.O.

TITLE: On the Chain Characteristics of Surface Reactions

PERIODICAL: V sb.: Probl. fiz. khimii. Nr 1, Moscow, Goskhimizdat, 1958, pp 4-100

ABSTRACT: Considering the ability of Pd to pass H_2 in the form of atoms (or H^+ ions), the authors developed a method for studying the mechanism of the heterogeneous catalytic reaction with the participation of H_2 . The reaction was carried out in a flow-circulation system on one (reaction) surface of the Pd-membrane (M), onto which at the same time can enter H atoms from the other (supply) side of the M. The dependence of the reaction rate on the quantity of H atoms passing through M is determined. The obtained data admits of determining the length of the chain $n = (v - v^0)/x(v^0 - \text{reaction rate in the absence of H flow through M}, v - \text{reaction rate at the speed of H overflow through M, equal to } x), \text{ and also the mean consumption of H atoms per one molecule of reaction product } v'$. For the hydrogenation of C_2H_4 at $20^\circ C$, $n = 0.3 - 0.5$ and $1 < v' < 3$; at $175^\circ C$, $n = 0$ and $v' < 0.25$. The values of v' and n at $20^\circ C$ show that the reaction proceeds by means of the consecutive addition of adsorbed H atoms. The values of v' and n

Card 1/2

On the Chain Characteristics of Surface Reactions

SOV/81-59-16-56444

at 175°C agree with the proposition that the reaction is a chain reaction, i.e., includes the stage C_2H_5 (ads.)+ H_2 = C_2H_6 +H(ads.), in which case the processes of formation and rupture of the chains $H_2 = 2H$ (ads.) take place more frequently than the processes of chain development. Another possible explanation is, that parallel with the mentioned reaction the process C_6H_4 (ads.)+ H_2 = C_2H_6 takes place. The mentioned data show that at an increase of the temperature the mechanism of the reaction changes: the H_2 molecules start taking part in it.

L. Apel'baum.

Card 2/2

TEMKIN, M.I.; APEL'BAUM, L.O.

Chain characteristics of surface reactions. Probl.fiz.khim.
no.1:94-100 '58. (MIRA 15:11)

1. Laboratoriya khimicheskoy kinetiki Nauchno-issledovatel'skogo
fiziko-khimicheskogo instituta im. Karpova.
(Catalysis)
(Chemical reaction, Rate of)

TEMKIN, M. I.

AUTHORS:

Kurilenko, A. I., Kul'kova, N. V.,
Rybakova, N. A., Temkin, M. I.

76-32-4-11/43

TITLE:

The Oxidation of Ethylene to Ethylene Oxide on a
Silver Catalyst (Okisleniye etilena v okis' etilena na se-
rebryanom katalizatore).
I. Experimental Investigation of the Reaction Kinetics
I. Eksperimental'noye izuchenije kinetiki reaktsii)

PERIODICAL:

Zhurnal Fizicheskoy Khimii, 1958, Vol. 32, Nr 4,
pp. 797-805 (USSR)

ABSTRACT:

Since the hitherto made investigations of the reaction mentioned in the title supplied different contradicting results the investigations mentioned in this paper were carried out by means of the method of continuous circulation. This method offers the following advantages: The reaction velocity is measured directly as function of the concentrations. The desired temperature in the reaction zone is secured in spite of the great heat effect of the process. Any form of catalyst can be used, without making it possible to the gas to pass by without touching

Card 1/4

The Oxidation of Ethylene to Ethylene Oxide on a
Silver Catalyst. I. Experimental Investigation of the
Reaction Kinetics

76-32-4-11/43

the catalyst. The possibility of the formation of external diffusion effects is reduced. From the experimental part from a diagram can be seen among other that the reaction vessel is a vertical glass tube in which the catalyst is located (spongy silver in form of tablets). A circular glass tube connected to the reaction vessel and a circulation pump introduce the gas mixture or drain it. Mostly the obtained ethylene oxide was frozen at -78°C and determined according to Lubatti (Reference 9). The results obtained show among other that in the first 70-80 hours the activity of the catalyst decreases and the selectivity increases (shown graphically). The two reaction velocities of ethylene oxide formation and of carbon dioxide and water formation are dealt with separately. The experiments were carried out with different gas concentrations, that is to say, ethylene 0.6 - 70%, oxygen 1.5 - 90%, ethylene oxide 0.3 - 3%, carbon dioxide 0.1 - 85% in order to determine the reaction kinetics. The results obtained are mentioned on some tables for different cata-

Card 2/4

The Oxidation of Ethylene to Ethylene Oxide on a
Silver Catalyst. I. Experimental Investigation of
the Reaction Kinetics

76-32-4-11/43

lyst samples. The two above mentioned reactions show reaction velocities which are calculated according to analogous equations. The observation that the freezing of ethylene oxide within the cycle does not change selectivity is in coincidence with some other references; the contradiction to the data by O. M. Todes and T. I. Andrianova (Reference 4) is explained by the longer contact time used by them. An impeding effect of the oxidation products on both reaction velocities was observed. The statement that in freezing ethylene oxide and water the reaction velocity sharply increases was already mentioned by Ya. B. Gorokhovatskiy and M. Ya. Rubanik (Reference 11). The raise of temperature effected a decrease in the yield of ethylene oxide. The activation energies were calculated and mentioned to be 15200 cal for the formation of ethylene oxide and 19800 cal for the formation of carbon dioxide and water. There are 6 figures, 7 tables and 11 references, 7 of which are Soviet.

Card 3/4

The Oxidation of Ethylene to Ethylene Oxide on a
Silver Catalyst. I. Experimental Investigation of the
Reaction Kinetics

76-32-4-11/43

ASSOCIATION: Fiziko-khimicheskiy institut im. Karpova, Moskva
(Moscow Physicochemical Institute imeni Karpov)

SUBMITTED: December 1, 1956

AVAILABLE: Library of Congress

1. Ethylene--Oxidation 2. Silver catalysts--Applications

Card 4/4

TEMKIN, M. I.

76-32-4-21/43

AUTHORS: Taybina, Ye. N., Gel'bshteyn, A. I., Arrest-Yakubovich, A. A.,
Temkin, M. I.

TITLE: The Kinetics of the Vapor Phase Hydration of Acetylene in the
Presence of a Carbon-Supported Phosphoric Acid Catalyst
(Kinetika parofaznoy gidratatsii atsetilena v prisutstvii
katalizatora - fosfornaya kislota na ugle)

PERIODICAL: Zhurnal Fizicheskoy Khimii, 1958, Vol. 32, Nr 4,
pp. 856 - 863 (USSR)

ABSTRACT: Investigations in the field of acetylene hydration were already
carried out by A. P. El'tekov (Reference 1), M. G. Kucherov
(Reference 4-6) and others so that the present paper is a
continuation of a previous one by A. Ya. Yakubovich, A. A.
Danilevich and N. A. Medzykhovskaya (Reference 9). Externally
there is apparently present an heterogenous catalytic process;
in fact it is an homogenously catalytic process which takes
place in liquid dissolved acetylene. From the technique applied
can be seen that the authors used the passage system within

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76-32-4-21/43

The Kinetics of the Vapor Phase Hydration of Acetylene in the Presence of
a Carbon-Supported Phosphoric Acid Catalyst

a temperature interval of from 261 - 302°C and with using activated charcoal BAU ; the catalyst was produced of this according to a method by N. M. Chirkovyy. From the results obtained can among other facts be seen that no retardation of diffusion of the process takes place and that the reaction velocity at a constant phosphoric acid concentration corresponds to an equation of first order. The increase of the pressure of steam leads to a decrease of the reaction velocity which is explained by the dilution of the acid. It was observed that parallel to the hydration an acetylene polymerization and croton condensation of acetaldehyde takes place. A. L. Klebanskiy and V. D. Titov (Reference 18) investigated the reaction mechanism of unsaturated compounds which were catalyzed by strong acids; they did this by investigating the alkylic acids formed as intermediate products. The hydration velocity of acetylene is proportional to its concentration as well as to the acidity of the medium and is dependent on the activity of water. This is

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explained by a monomolecular conversion of the product of proton addition to the acetylene molecule as reaction limit. The products are regarded as α -complexes of acetylene with a proton in the carbonium ion. Concluding from this a reaction scheme is given and the activation energy is calculated taking into account the temperature dependence of the activity of the catalyst. There are 1 figure, 3 tables, and 21 references, 14 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moskva (Moscow Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: December 27, 1956

AVAILABLE: Library of Congress

1. Acetylene--Hydration 2. Phosphoric acid--Catalytic properties

Card 3/3

AUTHORS: Tsybina, Ye. N., Gelbshteyn, A. I. Temkin, M. I. 76 32 5-5/4?

TITLE: The Kinetics of the Vapor Phase Hydration of Acetylene on Zinc Phosphate (Kinetika parofaznoy hidratacii atsetilena na fosfate tsinka)

PERIODICAL: Zhurnal fizicheskoy khimii, 1958, Vol. 32, Nr 5, pp 995-1002 (USSR)

ABSTRACT: The reaction kinetics were investigated according to the flow circulation method, which made possible an isothermal catalyst layer independent of the conversion degree of the reacting substances, and also made possible a direct measuring of the reaction velocity. The mechanism of the catalytic effect of protonic and aprotic acids or acid-similar substances, respectively, is assumed according to the terminology by A. I. Shatenshteyn (Ref 5). The experimental technique and the equipment are given. It was observed that the reaction took place in the kinetic range and that it did not depend on the granular size of the catalyst, but that it depended on the conditions of preparation, so that comparisons were made only with catalysts of the same series of production. The catalyst activity de

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creased with the prolongation of the working period which made necessary its regeneration after a certain working period. The amount of side reaction products was determined by bromination and served for orientation. As was shown by the results mentioned in form of tables the reaction velocity does not change with the partial pressure of the acetaldehyde, with the reaction kinetics corresponding to that of the catalytic effect of phosphoric acid; this permits to conclude on a similarity of the mechanism of the two catalysts. It is assumed that a corresponding carbonium ion of Zn^{+2} is formed the structure of which corresponds to that of the compound of mercury chloride with acetylene as assumed by A. N. Nesmeyanov and R. Kh. Freydlina (Ref 12) in the reaction of vinyl derivatives, and which is in the present case represented by $HC^+ = CHZn^+$. The productions by A. L. Klebansiy and V. D. Titov (Ref 14) based on the investigation results by A. N. Nesmeyanov, as well as those by Lyuderi and Tsuffanti (Ref 13) are also mentioned. Concluding the authors state that the formation velocity of acetaldehyde is proportional to the partial pressure of acetylene and independent of the partial pressure of water.

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and acetaldehyde, and that the yield of acetylene polymers is proportional to the ratio $P_{C_2H_2} / P_{H_2O}$.

There are 3 figures, 6 tables, and 15 references, 14 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L.Ya. Karpova, Moskva
(Moscow Physical-Chemical Institute imeni L.Ya. Karpov)

SUBMITTED: December 28, 1956

- 1. Acetylenes--Chemical reactions
- 2. Zinc phosphates--Chemical reactions
- 3. Chemical reactions--Velocity
- 4. Acids--Catalytic properties

Card 3/3

76-32-5-13/47

AUTHORS: Kurilenko, A. I., Kul'kova, N. V., Rybakova, N. A., Temkin, M. I.

TITLE: The Oxidation of Ethylene to Ethylene Oxide on a Silver Catalyst (Okisleniye etilena v okis' etilena na serebryanom katalizatore) II. Evaluation of the Reaction Kinetics (Dobsuzhdeniye kinetiki reaktsii)

PERIODICAL: Zhurnal fizicheskoy khimii, 1958, Vol. 32, Nr 5, pp. 1043 - 1048 (USSR)

ABSTRACT: Continuing earlier investigations in which contradicting results had been obtained the authors found that after the quick oxygen adsorption and formation of a monomolecular layer a process of slow adsorption follows which spreads over hundreds of hours, which was called the "deep chemical adsorption". It is dependent on the increased solubility of the oxygen in the silver layer below the surface. The slow change of the deeply adsorbed oxygen related to this is formed by the change of the activation of the catalyst, which fact is in agreement with the data by Orzechowski and MacCormak (Reference 4) as well

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Silver Catalyst. II. Evaluation of the Reaction Kinetics 76-32-5-13/47

as with the observations already made. This way two types of dependence of the kinetics can be assumed: the kinetics in a steady state of the catalyst, and that in a standard state, with different conditions of experiments having to be applied. The present investigations refer to the second case, and it is assumed that the reaction velocity does not depend on the oxygen pressure. Corresponding to the data by L. Ya. Margolis and S. Z. Roginskiy (Reference 5) it is assumed that as intermediate product vinylalcohol is formed which then oxidizes to CO_2 ; a diagram of the reaction mechanism in ionic form is mentioned. In the deduction of the kinetic equations the effect of the water is neglected and two final formulae of the reaction kinetics are determined. The influence of an increased ethylene concentration in the gas phase is explained by the decrease of the tendency to reach the concentration equilibrium of the deeply adsorbed oxygen and that on the surface, with other possibilities being mentioned as well. For an ethylene oxidation in a flow system an equation is obtained by integration, and an explanation is given for the differences of the

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The Oxidation of Ethylene to Ethylene Oxide on a 76-32-5-13/47
Silver Catalyst. II. Evaluation of the Reaction Kinetics

results of (Reference 4). There are 6 references, 4 of which
are Soviet.

ASSOCIATION: Fiziko-химicheskiy institut im. L. Ya. Karpova, Moskva
(Moscow Institute of Physics and Chemistry imen L. Ya. Karpov)

SUBMITTED: December 1, 1956

1. Ethylene--Oxidation
2. Oxygen--Adsorption
3. Silver--
Adsorptive properties
4. Silver catalysts--Performance
5. Mathematics--Applications

Card 3/3

5(4)

AUTHORS:

Bulatnikova, Yu. I., Apel'baum, L. O. SOV/76-32-12-10/32
Temkin, M. I.

TITLE:

The Poisoning of Ammonia Synthesis Catalysts by Hydrogen Sulfide, Traced With Radioactive Sulfur (Izuchenie otravleniya katalizatora sinteza ammiaka serovodorodom s primeneniyem radiosery)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1958, Vol 32, Nr 12,
pp 2717 - 2724 (USSR)

ABSTRACT:

The effect of H_2S on iron catalysts activated by Al_2O_3 , $Al_2O_3 + K_2O$ or K_2O alone was investigated. The effect on the $Fe + Al_2O_3$ catalyst is most easily explained. The poisoning is irreversible. Failure of the poisoning to ensue when 20% of the surface are covered with sulfur corresponds to the concept of surface effects, according to which the ammonia synthesis results predominantly in places with medium adsorption capacity. Therefore, the synthesis is, at first, not influenced by covering the strongly adsorbing points. Since, however, the weakly adsorbing

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points do not participate in the synthesis reaction either, complete poisoning sets in when 80% of the surface are covered with sulfur. The formation of a monoatomic layer suffices for poisoning. With the $Fe+Al_2O_3+K_2O$ catalyst a temporary poisoning can be observed when less than 20% of the surface are covered with sulfur. Perhaps this can be explained by the uneven distribution of the sulfur due to the reduced mobility of the S-atoms. Generally speaking, this catalyst is not so easily poisoned as the simpler $Fe+Al_2O_3$ catalyst.

Probably K_2O reacts with H_2S which explains the high resistivity against poisoning. In this case potassium is bound as $KAlO_2$, is not volatile, but still binds the hydrogen sulfide. The $Fe+K_2O$ catalyst easily loses K_2O , or rather the potassium volatilizes and deposits on the wall as K_2S . While Al_2O_3 stabilizes the finely dispersed structure of the catalyst, K_2O causes a greater intensitivity

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The Poisoning of Ammonia Synthesis Catalysts by Hydrogen Sulfide, Traced With Radioactive Sulfur

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towards H_2S . The formation of the FeS-film on the surface of the $Fe+Al_2O_3+K_2O$ catalyst ceases when the layer has reached a thickness of about 40 Å. There are 6 figures, 2 tables, and 20 references, 12 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moskva
(Physico-Chemical Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED: July 31, 1957

Card 3/3

AUTHORS:

Gel'bshteyn, A. I., Temkin, M. I.

20-118-4-32/61

TITLE:

On the Determination of the Reaction Order From the
Acidity (Ob opredelenii poryadka reaktsii po kislotnosti)

PERIODICAL:

Doklady Akademii Nauk SSSR, 1958, Vol. 118, Nr 4,
pp. 740-743 (USSR)

ABSTRACT:

In the catalysis by concentrated acids the degree of the transition of the substrate B into the protonized form BH^+ is determined by the acidity of the medium, i.e. by the ability to deliver a proton, and also by the alkalinity of the substrate:

$C_{BH^+}/C_B = K h_0$. Thereby h_0 denotes the acidity of the medium and K - the constant of the equilibrium of the reaction $B + H^+ \rightleftharpoons BH^+$. It is possible that the equilibrium is established previous to the limiting stage $B + 2H^+ \rightleftharpoons BH_2^{2+}$. In that case the constant k of the velocity must be proportional to h_0^2 . The dependence of the constant k on h_0 is usually represented by the equation

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the Acidity

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$k = \text{const. } h_0^n$, where on the exponent n is graphically determined. By this means in the decomposition of benzoyl-formic-acid in sulfuric acid the value $n = 2$ was determined and it was concluded that the reaction comprises the combination of two protons. The authors investigated the kinetics of the decomposition of formic acid into carbon monoxide and water in the media $H_2SO_4-H_2O$ (from 80,7 to 98,2 % H_2SO_4) and $P_2O_5-H_2O$ (from 72,4 to 83,3 % P_2O_5 , i.e. in the domain of the so-called strong phosphoric acids). The acidity of the system $P_2O_5-H_2O$ passes through a maximum at a P_2O_5 -percentage of about 80 % in contrast to the system $H_2SO_4-H_2O$, where the acidity monotonously depends on the composition. The peculiarity of the system $P_2O_5-H_2O$ makes possible a better determination of the relation between the constant of the reaction velocity and the acidity. The shape of the curve for the system $P_2O_5-H_2O$ indicates the inapplicability of the equation $k = \text{const. } h_0^n$. Then the authors give a formula

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for k and for a proportionality coefficient, occurring in this formula. Finally $k = F(x)e^{-E(x)/RT}$ is obtained, whereby $F(x)$ is an observed factor and $E(x)$ is the observed activation energy. These terms here are specialized more exactly. A table contains the values of the quantity occurring in these terms for 200°C. The accuracy of the here given formulae is shortly discussed. The finding of n by means of the equation $\log F(x) = \log B + n \log \beta$ fundamentally is more correct than the determination by the equation $k = \text{const.} \cdot h^n$, but it imposes considerably higher demands on the experimental data. There are 2 figures, 2 tables, and 4 references, 2 of which are Soviet

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut
im. L. Ya. Karpova (Physical-Chemical Scientific Research
Institute imeni L. Ya. Karpov)

Card 3/4

On the Determination of the Reaction Order From
the Acidity

20-1184-32/61

PRESENTED: July 23, 1957, by A. N. Frumkin, Member, Academy of
Sciences USSR

SUBMITTED: July 16, 1957

AVAILABLE: Library of Congress

Card 4/4

5(4)
AUTHORS:Kurilenko, A. I., Kul'kova, N. V., Ostrovskiy, V. Ye.,
Temkin, M. I.

SOV/20-123-5-30/50

TITLE:

The Influence of Electrically Negative Elements on the
Catalytic Effect of Silver in the Oxidation of Ethylene
(Vliyaniye elektrootritsatel'nykh elementov na kataliticheskoye
deystviye serebra pri okislenii etilena)PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 5, pp 878-881
(USSR)

ABSTRACT:

The catalytic oxidation of ethylene to ethylene oxide
 $C_2H_4 + (1/2)O_2 = C_2H_4O$ is carried out on a surface of silver
at $200 - 300^\circ$. Small admixed quantities of chlorine compounds
increase the selectivity of the catalyst, i.e., they de-
crease the relative influence of the undesirable reaction
 $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$ without diminishing the degree of
conversion of ethylene. The applied methods of the kinetic
measurements were described in previous papers. The experiments
were carried out in an apparatus with circulating flow at
 1° atmosphere and 218° . The circulating ethylene air mixture
contained 2.5 ± 0.2 volume per cent C_2H_4 . The degree of con-

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The Influence of Electrically Negative Elements Upon the Catalytic Effect
of Silver in the Oxidation of Ethylene

version of the C_2H_4 on silver without impurities of Cl and S amounted to 50-60%. The sulphur compounds used were marked by S^{35} . Crude silver (which was produced by decomposition of Ag_2CO_3 in a flow of an ethylene-air mixture) was used as catalyst. The majority of the experiments was carried out by means of silver grains which had a specific surface of $\sim 1m^2/g$. Tabloids (tabletka) of $5 \cdot 3$ mm (specific surface $0.3 m^2/g$) were used, as well. ω , denotes the rate of the reaction $C_2H_4 + (1/2)O_2 = C_2H_4O$. First, experiments with tabloid catalyst were carried out, and H_2S was added continuously to the reacting mixture for 20-30 hours. In various experiments the concentration varied within the limits of 0.1 and 50 mg/m³. The activity of the catalyst increased by 10-20% after the addition of $3 \cdot 10^{-4} - 5 \cdot 10^{-4}$ atomic percent S to the catalyst. By this addition selectivity was increased from $s = 0.70$ to $s = 0.77$. Independently of the concentration of H_2S in the gaseous mixture, the oxidation of ethylene was

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The Influence of Electrically Negative Elements Upon the Catalytic Effect
of Silver in the Oxidation of Ethylene

nearly interrupted by the adding of more than 10^{-2} atomic per cent of sulphur to the catalyst. During the catalytic process, the majority of sulphur is contained as sulfate on the surface of the silver samples. This allows the calculation of the degree of covering θ of the surface from the total amount of sulphur. A diagram shows the results of the determination of the catalytic activity and of the selectivity of silver grains which had previously been treated with H_2S in a "boiling layer". The second diagram gives the data concerning the catalysts which were produced by the simultaneous deposition of Ag_2CO_3 and Ag_2S . Also in this case, small amounts of sulphur increase the activity of the catalyst. The results of the experiments with introduction of sulphur Na_2SO_4 and H_2SO_4 agree with the above-discussed results, they prove the activating and corroding effect of SO_4^- ions upon surfaces of silver. Admixtures of Cl_2 and HCl in concentrations

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The Influence of Electrically Negative Elements Upon the Catalytic Effect of Silver in the Oxidation of Ethylene

of ~ 2 mg/m³ after the introduction of $0.5 \cdot 10^{-2}$ atomic per cent Cl (with respect to Ag) decreased the activity of the catalyst by 5 times, and the selectivity increased from 0.70 to 0.76-0.80. Corrosion was partially reversible. Higher concentrations caused an irreversible corrosion. According to the above-discussed results, the increase of the catalytic effect of silver in selectivity caused by the introduction of silver (and chlorine) cannot be explained by a partial corrosion of the catalyst with respect to the undesired reaction $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$. There are 2 figures and 9 references, 8 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-Chemical Scientific Research Institute imeni L. Ya. Karpov)
PRESENTED: July 21, 1958, by A. N. Frumkin, Academician
SUBMITTED: July 15, 1958

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PHASE I BOOK EXPLOITATION SOV/4386

Moscow. Fiziko-khimicheskiy institut

Problemy fizicheskoy khimii; trudy, vyp. 2 (Problems in Physical Chemistry; Transactions of the Institute, no. 2). Moscow, Goskhimizdat, 1959. 202 p. 1,000 copies printed.

Editorial Board: Ya. M. Varshavskiy, Doctor of Chemical Sciences; G. S. Zhdanov, Doctor of Chemical Sciences; V. A. Kargin, Academician; Ya. M. Kolotyrkin, Doctor of Chemical Sciences (Resp. Ed.); S. S. Medvedev, Academician; S. Ya. Pshenzhetskiy, Doctor of Chemical Sciences; V. M. Cherednichenko, Candidate of Chemical Sciences; V. S. Chesalova (Editorial Secretary), Candidate of Chemical Sciences; Ed.: I. A. Myasnikov; Tech. Ed.: Ye. G. Shpak.

PURPOSE: This collection of articles is intended for physical chemists.

COVERAGE: The collection is the second issue of the Transactions of the Scientific Research Institute of Physical Chemistry imeni L. Ya. Karpov. It contains 17 articles which review

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Problems in Physical Chemistry (Cont.)

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research in many facets of physical chemistry, including reaction kinetics, crystallography, spectroscopy, free energy studies, investigations of radiation effects in chemical reactions, low temperature studies, etc. Figures, tables, and references accompany the articles.

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Problems in Physical Chemistry (Cont.)

SOV/4386

Kucera, J. . (Czechoslovakia), Ye. V. Barelko, L. I. Kartasheva, P. N. Komarov, and M. A. Proskurnin. Decomposition Products of Phenol Formed During the Radiolysis of Benzene in an Aqueous Solution

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10-18-60

5(4)

AUTHORS: Sokolova, D. F., Morozov, N. M.,
Temkin, M. I. SOV/76-33-2-37/45

TITLE: Kinetics of Ammonia Synthesis at Low Pressure and Under
Conditions of Diffusion Retardation (Kinetika sinteza ammiaka
pri nizkikh davleniyakh v usloviyakh diffuzionnogo tormozheniya)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 2, pp 471-479
(USSR)

ABSTRACT: The question of the influence of diffusion phenomena on the
rate of synthesis of ammonia was investigated for the first
time by V. A. Royter (Ref 1), and the most recent experiments
on this question (Refs 2-7) have showed that the diffusion
retardation must absolutely be considered. Investigations on
the role of the diffusion factors in the ammonia synthesis were
carried out by V. N. Shishkova, I. P. Sidorov and M. I. Temkin
(Ref 9) at pressures of 100-300 atm using industrial catalysts
and the flowing-through-circulation method. The present paper
shows that the character of the diffusion process in this
latter type of investigation is different at atmospheric or
lower pressures than at high pressures. As opposed to the

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Under Conditions of Diffusion Retardation

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method in reference 8 the flowing-through-circulation system has two circulation cycles (Fig 1). The reaction rate was determined from an amount of ammonia frozen out of a supplementary cycle. The catalyst used was a melted magnetite which had been treated with a nitrogen-hydrogen mixture and which had Al_2O_3 and K_2O added to it. The experiments were carried out by using a nitrogen-hydrogen mixture (in stoichiometric ratio) at $350-500^\circ$ and with pressures of 1.0, 0.5 and 0.25 atm at various rates of diffusion (Table 1). The reaction kinetics were investigated in the diffusion area on a uniformly spherical catalyst (diameter = 1.2 cm) at $50-500^\circ C$ and the above mentioned pressures with a rate of gas diffusion of $3000 - 15000 \text{ hour}^{-1}$. The experiments indicate two limiting cases for the course of the reaction: in terms of kinetics (small-grained catalyst) the yield of the catalyst is proportional to its volume and in terms of the inner diffusion (coarse-grained catalyst) the yield is proportional to the outer surface of the catalyst particle. A comparison of the results obtained with the small-grained catalyst (Table 3)

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with those obtained with the coarse-grained catalysts yield the value of $D^* = 1 \cdot 10^{-2} \text{ cm}^2/\text{sec}$ for the effective diffusion coefficient of ammonia in the catalyst pores, according to equation (14) and at 1 atm pressure. This value apparently corresponds to the transformation range between the Knudsen and the usual diffusion, and defines the limit of kinetic diffusion. Using D^* the maximum diameter of the catalyst which will still allow the synthesis to proceed without retardation can be calculated:

$$a_{\text{limit}} = \sqrt{D^* \tau} \quad (\tau = \text{time of contact})$$

There are 2 figures, 3 tables, and 13 references, 10 of which are Soviet.

ASSOCIATION: Akademiya nauk SSR, Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moskva (Academy of Sciences, USSR Physical-Chemical Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED: August 7, 1957
Card 3/3

5(4)

SOV/76-33-9-25/37

AUTHOR: Temkin, N. I.

TITLE: On Conditions for the Coexistence of Gaseous Phases

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 9,
pp 2040 - 2044 (USSR)

ABSTRACT: Van der Waals' theory of binary mixtures permitted a qualitative detection of equilibria in the gas-gas system (Ref 1) already before I. R. Krichevskiy, P. Ye. Bol'shakov, and D. S. Tsiklis (Refs 2-4) made experiments on this problem. It is shown that Van der Waals' theory allows for an explanation of many results published in the articles mentioned in references 2-4. The equation

$$(a_{12} = (a_1 a_2)^{1/2}) \quad (7)$$
 according to Galitzine-Berthelot (Refs 6,7)
$$a_{12}$$
 the constant characteristic of the gas mixture) cannot be applied to gas mixtures composed of an apolar and a strongly polar gas, and besides, a_{12} is temperature-dependent for polar gases. An excellent interpretation of Van der Waals' theory has been given by Lorentz (Ref 8), on the basis of which the author de-

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duced here the conditions of a gas-gas equilibrium in binary systems. The latter equilibrium occurs in binary systems only if constant a_{12} is far below the arithmetic mean of constants a_1 and a_2 . This condition is satisfied only by mixtures composed of a polar and an apolar gas, or by binary mixtures with helium as one component. In this manner, it is also possible to explain the limited ability of gases to be mixed with one another, as observed by experiments. There are 10 references, 7 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moskva
(Physico-chemical Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED: March 4, 1958

Card 2/2

5(4)
AUTHORS:Stroyeva, S. S., Kul'kova, N. V., Temkin, M. I.
SOV/20-124-3-38/67

TITLE:

The Isotopic Exchange Between Co and CO_2 on Various Surfaces
(Izotopnyy obmen mezhdu Co i CO_2 na razlichnykh poverkhnostyakh)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 3, pp 628-631
(USSR)

ABSTRACT:

In the reactions of isotopic exchange the regularities determining the specific catalytic effects of the surface must occur in a more simple form than in other catalytic heterogeneous processes. Therefore, the authors investigated the rate of isotopic exchange between Co and CO_2 on various surfaces by using C^{14} . In this way the reaction $\text{C}^{14}\text{O}_2 + \text{CO} = \text{C}^{14}\text{O} + \text{CO}_2$ was observed, which corresponds to the two-stage scheme $\text{C}^{14}\text{O}_2 + () = \text{C}^{14}\text{O} + (0)$, $\text{CO} + (0) = \text{CO}_2 + ()$. Here (0) denotes an oxygen atom on the surface, and () denotes a place of the surface which is free from oxygen. A formula is written down for the rate of reaction for the case in which the above-mentioned reaction takes place on the surface which

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is uniformly inhomogeneous with respect to the adsorption heats of oxygen. Besides, average degrees of covering are assumed. The kinetics of the equation described by the aforementioned equation was investigated in a static device with circulation. For the purpose of measuring the radioactivity of CO and CO_2 , the BaCO_3 -precipitates were investigated by means of a counter. An equation for calculating the constants of the rate of exchange is written down and explained. The catalysts used in the course of experiments had the shape of tablets (Ag, Cu, Pt, Co, Fe_3O_4 , Ni, W) with a diameter of 2-5 mm and of foils (Ag, Pt, Ni). The results obtained by measurements are shown by table 1. In the case of all catalysts (with the exception of Fe_3O_4) the reaction $\text{CO} + \text{MeO} \rightleftharpoons \text{Me} + \text{CO}_2$ is shifted practically completely in the direction of the production of metal. The aforementioned reaction could not be observed on tablet-shaped silver powder (175-350°) and on a silver foil (700°). For copper kinetic measurements were carried out within the temperature range of 250-400°. The quantity k remained constant with a variation of the total pressure $P = P_{\text{CO}} + P_{\text{CO}_2}$, and, under certain conditions, it

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does not depend on the composition of the mixture. In the case of platinum, also the reaction $2\text{CO} = \text{C} + \text{CO}_2$, the equilibrium of which is at $t < 700^\circ$ shifted towards the production of carbon, takes place parallel with the reaction mentioned above. Without a catalyst this reaction does not occur, but it develops at a considerable rate in the presence of Ni, Co, Fe, and also of Pt, as shown by the experiments carried out by the authors. On cobalt the aforementioned reaction becomes noticeable at 265° . In the case of nickel the activity of the catalyst was diminished by carbonization. Experiments with tungsten were carried out at $550-700^\circ$. The tungsten-phase showed only little stability in the case of the prevailing experimental conditions. Isotopic exchange was found to occur at temperatures of from 550° onwards; at this temperature also the formation of tungsten-carbide begins. At higher temperatures tungsten is oxidized by carbonic acid. The results obtained by measuring the specific surface of the catalysts on the basis of data concerning the adsorption of nitrogen at low temperatures are given by table 2. There are 2 tables and 11 references, 4 of which are Soviet.

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The Isotopic Exchange Between Co and CO_2 on Various Surfaces

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im.
L. Ya. Karpova
(Physico-Chemical Scientific Research Institute imeni L. Ya.
Karpov)

PRESENTED: September 29, 1958, by S. S. Medvedev, Academician

SUBMITTED: September 20, 1958

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5(4)

AUTHORS: Bakshi, Yu. M., Gel'bshteyn, A. I., Temkin, M. I. SOV/20-126-2-24/64

TITLE: The Equilibrium of the Synthesis of Ethyl Alcohol (Ravmoveniye sinteza etilovogo spirta)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 2, pp 314-317 (USSR)

ABSTRACT: The degrees of transformation attainable in the hydration of ethylene in the gaseous phase depend on the equilibrium $C_2H_4(gas) + H_2O(gas) \rightleftharpoons C_2H_5OH(gas)$. The gases participating in this equilibrium must never be considered to be perfect in the case of the industrial realization of this reaction. For this and other reasons the authors carried out an experimental investigation of the above-mentioned equilibrium, and the results obtained by these investigations are discussed in the present paper. The investigations were carried out in a proton reactor made of stainless steel. The catalyst in this case was silica-gel (~40% H_3PO_4 of the weight of the catalyst). Carrying out these experiments is described. The equilibrium was attained from two sides, and results were found to be in practical agreement. The experimental results are shown by a rather voluminous table. The velocities referred to the volume

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The Equilibrium of the Synthesis of Ethyl Alcohol

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were calculated as the ratio between the ethylene yields per hour (0°, 1 atm) and the volume of the catalyst layer. The average values of $K_p = \frac{P_{C_2H_5OH}}{P_{C_2H_4} P_{H_2O}}$ determined by means of experiments

carried out with mixtures of alcohol and water are also shown by a table. In this connection it holds that $P_{C_2H_5OH} = P_{C_2H_5OH}^{PM}$

(P - total pressure, $N_{C_2H_5OH}$ - molar fraction of C_2H_5OH). In the case of slight deviations from the perfect state, the equation of state of a gas mixture may be used: $V = \frac{RT}{P} + B$. Here V denotes the molar volume of the mixture, and B - the second virial coefficient, which depends upon the state of the mixture: $B = \sum_i \sum_j B_{ij} N_i N_j$. The quantities $B_{ij} = B_{ji}$ are functions of T. For the "activity coefficient"

$\gamma_i = \frac{f_i}{N_i P}$ it holds that $\ln \gamma_i = \frac{2B_i - B}{RT} - P$ with $B_i = \sum_j B_{ij} N_j$. With

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$$\ln K_P = \sum_i V_i \ln \gamma_i$$
 (where γ_i denote the stoichiometric coefficients)

there follows $\ln K_P = \frac{2 \sum_i V_i B_i - B \sum_i V_i}{RT} P$. The quantity $\frac{2 \sum_i V_i B_i - B \sum_i V_i}{RT}$ is a function of the state and of temperature, and in the case of T being given, depends only on the ratio $\frac{P_{H_2O}}{P_{C_2H_4}}$. $\ln K_P$ must

depend linearly on P . The calculations carried out in accordance with the methods discussed in the present paper show satisfactory agreement with the experiment, especially at high temperatures. There are 2 figures, 2 tables, and 23 references, 8 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-Chemical Scientific Research Institute imeni L. Ya. Karpov)
 PRESENTED: January 26, 1959 by S. S. Medvedev, Academician
 SUBMITTED: January 24, 1959
 Card 3/3

TEMKIN, M.I.; APEL'BAUM, L.O.

Use of a semipermeable membrane in the study of the chain characteristics
of surface reactions. Probl. kin. i kat. 10:392-397 '60.
(MIRA 14:5)

1. Fiziko-khimicheskiy institut imeni A.Ya. Karpova.
(Catalysis) (Palladium)
(Hydrogenation)

APEL'BAUM, L.O; BEREZINA, Yu.I. (TEMKIN, M.I. (Moscow)

Radiochemical study of the sulfur poisoning of a cobalt catalyst
employed in the oxidation of ammonia. Zhur. fiz. khim. 34 no.12:
2795-2803 D '60. (MIRA 14:1)

I. Fiziko-khimicheskiy institut imeni K.Ia. Karpova.
(Sulfur—Isotopes) (Cobalt oxide)

S/020/60/132/01/41/064
B004/B007AUTHORS: Bakshi, Yu. M., Gel'bshteyn, A. I., Temkin, M. I.TITLE: Additional Data on the Equilibrium of the Synthesis of Ethyl Alcohol

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 1, pp. 157-159

TEXT: In Ref. 1 the authors published the data on the equilibrium of the reaction (1) C_2H_4 gas + H_2O gas $\rightleftharpoons C_2H_5OH$ gas at pressures of up to 81 atm. They found the linear dependence of $\log K_p$ on total pressure, extrapolated $\log K_p$ for $P = 0$, and obtained equation (2): $\log K_f = 2093/T - 6.304$. In the present paper they report on the dependence of the logarithm of the coefficient K_f on P .

($K_f = \gamma_{C_2H_5OH}/\gamma_{C_2H_4}\gamma_{H_2O}$; γ - activity coefficient). The data is given in table 1. Further, equation (5) was derived from the dependence $K_p = K_f/K_f$. Table 2 compares the values of K_p calculated from this equation with the experimentally determined values. The degree of equilibrium α of the conversion of ethylene into alcohol,

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determined according to equation (6) with $\frac{N_{H_2O}}{N_{C_2H_4}} = 1$ is given in table 3,

and in table 4 α is given for 290° for a different ratio between water and ethylene. Calculation of the heat effect of reaction (1) gives $\Delta H = -5263$ cal at 300° and 80 atm, whereas $\Delta H^\circ = -9370$ cal. This dependence of ΔH on P must be taken into account for technical calculations. There are 4 tables and 1 Soviet reference. ✓

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Institute of
Physical Chemistry imeni L. Ya. Karpov)

PRESENTED: December 30, 1959, by S. S. Medvedev, Academician

SUBMITTED: December 30, 1959

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80489

S/020/60/132/02/39/067

B004/B007

5.7.200

AUTHORS: Gel'bshteyn, A. I., Bakshi, Yu. M., Temkin, M. I.TITLE: The Kinetics of the Hydration of Ethylene in the Vapor Phase on a Phosphoric Acid Catalyst

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 2, pp. 384-387

TEXT: The authors investigated the industrially utilized reaction $C_2H_4^{(gas)} + H_2O^{(gas)} = C_2H_5OH^{(gas)}$ (1). As catalyst, phosphoric acid applied to silica

gel was used. The authors proceeded from the assumption that the reaction develops in a way similar to the previously (Ref. 1) investigated hydration of C_2H_2 , and that only its reversibility must be taken into account. Scheme (2) is written down for reaction (1), and it is found that the transformation of the H^+ π -complex $H_2C\ddagger CH_2$ into the carbonium ion $H_3C-C^+H_2$ is the stage that limits the reaction rate. From scheme (2) equation (3) is derived for the direct reaction,

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The Kinetics of the Hydration of Ethylene in the
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after which equation (4) is obtained with some simplification: $v_1 = k_1 h_o P_{C_2H_4}$

(v_1 = rate of direct reaction, k_1 = reaction constant, h_o = acidity of H_3PO_4 ,
 $P_{C_2H_4}$ = partial ethylene pressure). In a similar manner, equation (5) is

obtained for the rate of reversible reduction, equation (7) is derived for the
total reaction, and finally equation (9) is written down for the constant k of
the total reaction. Table 1 gives the experimental data for absolute pressures P
between 36 and 81 atmos and a reaction temperature of 290°C. The values of k
remain constant within the limits of experimental errors. The low degree of
dependence of the alcohol yield upon P_{H_2O} proves the zeroth order of the

reaction with respect to water, which does not participate in the limiting
stage of the reaction. For technical purposes the reaction rate is represented
as an explicit function of P_{H_2O} . For the reaction constant k' one finds:

$k' = k P_{H_2O}^{1/2}$ (15). The values of k' given in Table 1 are approximatively constant.

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For the temperatures of 270, 290, 310, and 330°C as well as $P_{H_2O} = 30$ atmos,

the average values of k_1 and k' are given in Table 2. As in the adsorption of C_2H_4 and C_3H_6 in H_2SO_4 (Ref. 9), and in the hydration of C_2H_2 (Ref. 1) also in this case the transformation of the π -complex into the carbonium ion is the limiting stage. There are 2 tables and 9 references, 7 of which are Soviet.

ASSOCIATION: Fizichesko-khimicheskiy institut im. L. Ya. Karpova (Institute of Physical Chemistry imeni L. Ya. Karpova)

PRESENTED: December 30, 1959, by V. A. Kargin, Academician

SUBMITTED: December 21, 1959

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33488

S/195/61/002/005/013/027
E111/E485

5.1190

AUTHORS: Temkin, M.I., Nakhmanovich, M.L., Morozov, N.M.
TITLE: Kinetics and mechanism of isotope exchange and gas reacting on the surface of solids

PERIODICAL: Kinetika i kataliz, v.2, no.5, 1961, 722-726

TEXT: Use of isotopes as tracer atoms permits direct observation of the different stages in a catalysed reaction. The object of the present work was to illustrate, with simple examples, the relation between the kinetics of reactions on the surface of solids and the kinetics of isotope-exchange processes. The simplest heterogeneous catalysed reaction can be written as



where A and B are reactants, X and Y reaction products, () is a vacant site on the surface and (I) a chemisorbed intermediate particle. Addition gives the overall reaction



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E111/E485

Kinetics and mechanism ...

The cases considered are those of the reaction of watergas, on a magnetite catalyst at 400 to 500°C, the reaction of carbon with CO₂, the isotope exchange by oxygen or carbon between carbon mono- and dioxide, the exchange of deuterium between water vapours and hydrogen. All these reactions can be considered particular cases of a general equation. If the adsorbed intermediate obeys the Langmuir isotherm this equation is

$$\omega = \frac{x_1 p_A x_2 p_B - x_{-1} p_X x_{-2} p_Y}{x_1 p_A + x_{-1} p_X + x_2 p_B + x_{-2} p_Y} \quad (19)$$

where ω is the rate of the reaction, x_1 the rate constant of the first stage in the forward direction, x_{-1} that in the reverse direction (x_2 and x_{-2} same for the second stage), p_A the partial pressure of A (or the product of their partial pressures if several substances participate, and so on). If the intermediate compound adsorption follows a logarithmic isotherm, then

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Kinetics and mechanism ...

$$\omega = \frac{1}{f} \cdot \frac{\pi}{\sin \alpha \pi} \cdot \frac{x_1^0 p_A x_2^0 p_B - x_{-1}^0 p_X x_{-1}^0 p_Y}{(x_1^0 p_A + x_2^0 p_Y)^c (x_{-1}^0 p_X + x_{-2}^0 p_B)^{1-c}}. \quad (20)$$

Here x_1^0 is the value of x_1 at the greatest adsorption energy of the intermediate compound, and so on; α is the proportionality coefficient between the change in the adsorption energy and the activation energy; f is the ratio of the adsorption-energy change range to RT . Both equations correspond to steady-state conditions. Eq.(20) is supported by some experimental data at medium degrees of surface coverage by the intermediate compound (e.g. Ref.4: V.A.Yevropin, N.V.Kul'kova, M.I.Temkin, Zh. fiz. khimii, v.30, 1956, 348). The authors report unpublished work on the reaction $\text{HDO} + \text{H}_2 \rightleftharpoons \text{HD} + \text{H}_2\text{O}$ in a flow system with water containing 2.2 or 2.5 atomic % deuterium. Since $\text{PHDO} \ll \text{PH}_2\text{O}$ and $\text{PHD} \ll \text{PH}_2$, it follows from Eq.(20) that for this reaction

$$\omega = k_1 p_{\text{HDO}} \left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \right)^m - k_2 p_{\text{HD}} \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right)^{1-m}. \quad (22)$$

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whereby $m = a$. Integration after substituting $dP_{HDO}/d\tau$ for ω (where τ is the contact time) gives

$$k_1 (p_{H_2}/p_{H_2O})^{m-1} = \frac{\ln \frac{|D|_{H_2O}/|D|_{H_2} + p_{H_2}/p_{H_2O}}{|D|_{H_2O}/|D|_{H_2} - K^{-1}}}{\tau (p_{H_2}/p_{H_2O} + K^{-1})} \quad (23)$$

Here $K = k_1/k_2$ is the equilibrium constant for the reaction. The equation was verified by the fact that linear relations were obtained between $\log k_1 (p_{H_2}/p_{H_2O})^{m-1}$ and $\log p_{H_2}/p_{H_2O}$ at constant temperatures for a variety of catalysts (porous nickel, nickel foil, porous cobalt, palladium foil, porous copper, porous silver, porous ferrous-ferric oxide). The values of m obtained were little dependent on temperature and were 0.5, 0.6, 0.3, 0.3, 0.8 and 0.8 to 1.0 for Ni, Co, Pd, Cu, Ag and Fe_3O_4 respectively. This sequence of catalysts also corresponds to the sequence of the absolute rate constant values, i.e. those calculated per unit surface. In order of magnitude, the absolute rate constant for deuterium exchange between water vapour and hydrogen or magnetite coincides with that for isotope exchange between carbon and carbon

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dioxide at the same temperature. It was previously shown (Ref. 3: N.V.Kul'kova, E.D.Kuznets, M.I.Temkin, Dokl. AN SSSR, v.90, 1953, 1067) that the latter similarly coincides with that for the water-gas reaction. This confirms the stepwise catalysis mechanism. D.A.Frank-Kamenetskiy and A.F.Semechkova are mentioned in the paper. There are 1 figure and 8 Soviet bloc references.

ASSOCIATION: Fiziko-khimicheskiy institut im, L.Ya.Karpova
(Physicochemical Institute im. L.Ya.Karpov)

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APEL'BAUM, L.O.; TEMKIN, M.I.

Mechanism of the catalytic hydrogenation of ethylene. *Zhur.fiz.khim.* 35 no.9;2060-2070 '61. (MIRA 14:10)

1. Fiziko-khimicheskiy institut imeni L.Ya. Karpova, Moskva.
(Ethylene) (Hydrogenation)

OSTROVSKIY, V.Ye.; KUL'KOVA, N.V.; LOPATIN, V.L.; TEMKIN, M.I.

Modifying action of additives on the ethylene oxidation catalyst.
Kin.i kat. 3 no.2:189-193 Mr-Ap '62. (MIRA 15:11)

1. Fiziko-khimicheskiy institut imeni L.Ya.Karpova.
(Ethylene) (Oxidation) (Catalysts)

KURILENKO, A.I.; KUL'KOVA, N.V.; BARANOVA, L.P.; TEMKIN, M.I.

Kinetics of ethylene catalytic oxidation. Kin.i kat. 3
no.2:208-213 Mr-Ap '62. (MIRA 15:11)

1. Fiziko-khimicheskij institut imeni L.Ya.Karpova.
(Ethylene) (Oxidation) (Catalysis)

TEMKIN, M.I.

Gradientless methods for determining reaction rates. Kin.i kat.
3 no.4:509-517 Jl-Ag '62. (MIRA 15:8)

1. Fiziko-khimicheskiy institut imeni L.Ya.Karpova.
(Chemical reaction, Rate of)

BLYUMENFEL'D, L.A.; TEMKIN, M.I.

Possible mechanism of the formation of adenosinetriphosphoric acid in the course of oxidative phosphorylation.
Biofizika 7 no.6:731-733 '62. (MIRA 17:1)

1. Institut khimicheskoy fiziki AN SSSR, Moskva i Fiziko-khimicheskiy institut im. L.Ya. Karpova, Moskva.

POLING, Laynus [Pauling, L.], prof. (SShA); Redaktor perevoda: TEMKIN, M.I.

Theory of resonance in chemistry. Zhur. VKHO 7 no.4:462-467
'62. (MIRA 15:8)
(Mesomerism)

TEMKIN, M.I.; MOROZOV, N.M.; SHAPATINA, Ye.N.

Ammonia synthesis when moving off equilibrium. Part 2.
Kin. i kat. 4 no.2:260-269 Mr-Ap '63.

(MIRA 16/5)

1. Fiziko-khimicheskiy institut imeni L.Ya.Karpova.
(Ammonia) (Iron catalysts)
(Phase rule and equilibrium)

TEMKIN, M.I.; MOROZOV, N.M.; SHAPATINA, Ye.N.

Kinetics of ammonia synthesis reaction carried away from equilibrium. Kin. i kat. 4 no.4:565-573 Jl-Ag '63. (MIRA 16:11)

1. Fiziko-khimicheskiy institut imeni L.Ya.Karpova.

TAYKHERT, A.M.; MOROZOV, N.M.; TEMKIN, M.I.

Kinetics of tritium exchange between water vapor and hydro-
gen on a nickel catalyst. Kin. i kat. 4 no.6:904-909 N-D '63.
(MIRA 17:1)

1. Fiziko-khimicheskiy institut imeni Karpova.